Immobilization of β-cyclodextrin onto Dowex resin as a stationary microvessel and phase transfer catalyst

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1. Introduction

The use of cyclodextrins (CDs) as microvessels to perform chemical reaction has attracted the interest of chemist since the 1960s [1]. Cyclodextrins have hydrophobic cavities into which organic molecules of appropriate size and shape can be incorporated mainly through hydrophobic interactions in aqueous solutions [2–5]. Although water has many unique properties, it has not traditionally been the solvent of choice in which to perform organic reactions. One reason has been that the nonpolar nature of organic molecules results in low or no solubility in water [6].

As is well known, the solubility of apolar guest compounds in water is (in general) increased when they form inclusion complexes with CDs [7–11]. Thus, cyclodextrins are potent phase transfer catalysts (PTC) [12,13].

On the other hand, the practical utility of CDs could be extended further if they can be rendered water soluble. Different strategies have been explored in the literature including polymerization procedures and immobilization onto solid particles such as silica, PEGylated Merrifield resins, and inside nanoporous oxides [14–16].

Immobilization of the phase transfer catalyst on an insoluble polymeric matrix has considerable advantages. Not only would the catalyst recovery and product isolation be greatly simplified but also, owing to the three-phase nature of the system, continuous flow methods could be employed, making the technique particularly attractive for industrial applications [17].

Recently, as part of our efforts to introduce novel PTC systems for the synthesis of organic compounds [18,19]; we have reported grafting of the poly(ethylene glycol) onto Dowex resins [20], as an efficient and reusable catalyst in the regioselective azidolysis of epoxides in water. Taking into account all this; we decided to immobilize β-CD as a stationary microvessel and new phase transfer system for organic transformation.

2. Experimental

2.1. General remarks

Epoxides and other chemical materials were purchased from Fluka and Merck and used without further purification. Dowex H+ resin (mesh 30–40) was washed with cold methanol, dried under vacuum at 50 °C and stored in an airtight container. β-cyclodextrin was heated at 80 °C under vacuum for 30 min before use to remove traces of moisture. Products were characterized by comparison of their physical data, IR and 1H NMR spectra with known samples. NMR spectra were recorded in CDCl3 on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as internal standard. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. GLC analyses were performed on a Shimadzu GC-12 A chromatograph equipped with a 3-m Thermon-1000 column.

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2.2. Typical procedure for immobilizing of β-cyclodextrin to Dowex Maraton C

An oven dried 50 mL flask equipped with a magnetic stirrer is charged with dried Dowex H+ resin (2 g) under nitrogen atmosphere. Then freshly distilled SOCl2 (5.0 mL, 67 mmol) was added slowly to the flask through an addition funnel and the reaction mixture was stirred under reflux conditions. After stirring for 6 h, the excess unreacted thionyl chloride was distilled out. Under nitrogen atmosphere, a solution of freshly dried β-cyclodextrin (3.4 g, 3 mmol) in dried pyridine (10 mL) was added dropwise to the resulting polymer. The solution was mixed at room temperature until no HCl was produced. The solid was filtered off and washed thoroughly with acetone and water. Then, the Dowex-β-CD was collected and dried in vacuum.

2.3. Typical procedure for the ring opening of epoxides

NaBH4 (4.0 mmol) was added gradually to a mixture of epoxide (1.0 mmol) and Dowex-β-CD (0.1 g) in water (5.0 mL). The suspension was magnetically stirred at room temperature for the time shown in Table 2. After complete consumption of epoxide as judged by TLC (using n-hexane/ethylacetate (5:1) as eluent), the insoluble PTC was filtered off and the filtrate was extracted with ether (3 × 5). The extract was dried over Na2SO4 and evaporated in vacuo to give the alcohols. The crude products were purified by silica gel column chromatography.

3. Results and discussion

β-CD, a cyclic oligosaccharide composed of seven α-(1→4) linked D-glucopyranose units [21,22], can be easily immobilized to Dowex Maraton C resin in the reaction depicted in Scheme 1. In the first step, sulfonic acid functional groups of resin were converted to sulfonyl chloride. Cyclodextrin can be efficiently immobilized on the resin by reaction of sulfonyl chloride functional groups with β-CD. The reaction is very clean and does not require any work-up procedure because the evolved HCl gas can be removed from the reaction vessel immediately.

To determine the amount of β-CD supported on the resin, 0.5 g of the each resins, Dowex-SO3H and Dowex-β-CD, were washed with methanol, dried and mixed with 20 mL of 0.5 M NaOH for 1 h. Then, the solutions were titrated with 0.5 M NaOH solution and the reduction of 2, 3-epoxypropyl phenyl ether under similar reaction condition, without adding catalyst, the substrate did not react with NaBH4, even after two days and more than 90% of the substrate was recovered.

An oven dried 50 mL flask equipped with a magnetic stirrer is charged with dried Dowex H+ resin (2 g) under nitrogen atmosphere. Then freshly distilled SOCl2 (5.0 mL, 67 mmol) was added slowly to the flask through an addition funnel and the reaction mixture was stirred under reflux conditions. After stirring for 6 h, the excess unreacted thionyl chloride was distilled out. Under nitrogen atmosphere, a solution of freshly dried β-cyclodextrin (3.4 g, 3 mmol) in dried pyridine (10 mL) was added dropwise to the resulting polymer. The solution was mixed at room temperature until no HCl was produced. The solid was filtered off and washed thoroughly with acetone and water. Then, the Dowex-β-CD was collected and dried in vacuum.

Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Isolated yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dowex-β-CD</td>
<td>8</td>
<td>100</td>
<td>40 (1a), 55 (1b)</td>
</tr>
<tr>
<td>2</td>
<td>Dowex</td>
<td>8</td>
<td>40</td>
<td>12 (1b and some diol was isolated)</td>
</tr>
<tr>
<td>3</td>
<td>–</td>
<td>48</td>
<td>10</td>
<td>5 (1b)</td>
</tr>
<tr>
<td>4</td>
<td>Dowex-β-CD’</td>
<td>12</td>
<td>100</td>
<td>70 (1a), 15 (1b)</td>
</tr>
</tbody>
</table>

*Inactivated sites resins.*
In conclusion, we have described an efficient method for the immobilization of β-cyclodextrin onto a polymer matrix. Dowex-β-CD was objectified and evaluated as a heterogeneous catalyst by the reduction of epoxides to the corresponding alcohols with sodium borohydride, and was found to exhibit good activity. Extensive research to use this solid–liquid phase transfer catalyst system in organic transformation is currently underway in our group and will be reported in due course.

Acknowledgement

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References


Table 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>Epoxide</th>
<th>Product(s)a</th>
<th>Time (h)</th>
<th>Yield (%)b</th>
<th>Yield (%)c</th>
</tr>
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<tr>
<td>1</td>
<td>PhO</td>
<td>PhO</td>
<td>8</td>
<td>40(55)f</td>
<td>40(55)f</td>
</tr>
<tr>
<td>2</td>
<td>Ph</td>
<td>OH</td>
<td>6</td>
<td>40(50)f</td>
<td>40(50)f</td>
</tr>
<tr>
<td>3</td>
<td>PhO</td>
<td>PhO</td>
<td>8</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PhO</td>
<td>PhO</td>
<td>12</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>PhO</td>
<td>PhO</td>
<td>24</td>
<td>10</td>
<td></td>
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</tbody>
</table>

* Products were identified by comparison of their physical and spectral data with those of authentic samples.
* Isolated yields.
* According to GLC analysis.

Acknowledgement

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